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MEASUREMENT AND CORRELATION OF THE SOLUBILITY AND DIFFUSION COEFFICIENT FOR OXYGEN AND CHLORINE IN BASIC HYDROGEN PEROXIDE

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Final Report

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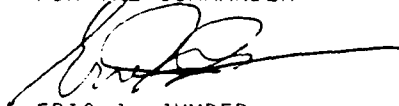This technical report has been reviewed and is approved for publication.

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The objective of this research was to determine the solubility and diffusivity of oxygen and chlorine in basic hydrogen peroxide. The solubility of O_2 in aqueous H_2O_2[35 % (wt)] was measured directly in a solubility apparatus over the temperature range -10 to 20°C. The data may be expressed in terms of Henry's law as

$$\ln H(atm\ 1/gmol) = 15.626 - 2587/T(K)$$

The solubility of chlorine in aqueous H_2O_2 could not be measured directly because of the reaction between Cl_2 and H_2O_2. However, solubility parameters which would allow the prediction of the solubility of Cl_2 and O_2 in basic hydrogen peroxide were either estimated from literature data or measured in the laboratory.

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19. ABSTRACT (Continued)

The diffusivity of chlorine in aqueous hydrogen peroxide [33 (wt)] was measured in a laminar liquid jet apparatus. The data were obtained over a temperature range -10 to 20°C and were correlated by

$$D\ (cm^2/s)\ =\ (-1.9038 \times 10^{-5}) + (8.18 \times 10^{-3})\ T(K)$$

The diffusivity of O_2 in aqueous hydrogen peroxide was measured in a wetted sphere absorber. Data were obtained over a temperature range -8 to 12°C and were correlated by

$$D(cm^2/s) = (-1.6552 \times 10^{-4}) + (6.3259 \times 10^{-7})\ T(K)$$

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FIGURES

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1.0 INTRODUCTION

The reaction between chlorine (Cl$_2$) and basic hydrogen peroxide [BHP, a mixture of hydrogen peroxide (H$_2$O$_2$) and potassium hydroxide (KOH)],

$$Cl_2 + H_2O_2 + 2KOH \longrightarrow 2KCl + 2H_2O + O_2(^1\Delta_g) \tag{1}$$
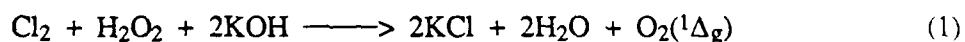
is currently being utilized to provide a source of singlet delta oxygen [O$_2$($^1\Delta_g$)] for iodine (I*) chemical lasers. The byproducts of the reaction in Equation 1 are potassium chloride (KCl) and water (H$_2$O). Typically an excess of hydrogen peroxide is used. The physical solubilities and liquid diffusion coefficients of oxygen (O$_2$) and Cl$_2$ in BHP are important physicochemical parameters needed to model any generator designed to produce singlet delta oxygen based on the reaction between gaseous Cl$_2$ and BHP solutions.

The objective of this research is to measure and correlate the solubility and diffusion coefficient for oxygen and chlorine in aqueous alkaline hydrogen peroxide solutions, in the range of -20 to 20 ºC. The solution of interest for this work is an aqueous solution of 5 molar potassium hydroxide and 8 molar hydrogen peroxide (5 M KOH, 8 M H$_2$O$_2$ and 30 M H$_2$O). This concentration of solution could be achieved by adding solid KOH to a 33 percent (wt) solution of hydrogen peroxide.

The gas solubilities are measured in an apparatus in which a known volume of degassed liquid is brought into contact with the gas in a closed system at constant temperature and pressure. The amount of gas absorbed at equilibrium is measured volumetrically.

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The diffusivities of Cl_2 and O_2 in aqueous H_2O_2 solutions are measured in two devices, a laminar liquid jet absorber and a wetted-sphere absorber, respectively. The principle idea for both of these devices is that the gas absorption rate is measured for a system in which the liquid phase fluid dynamics are known. The diffusion coefficient is calculated from the measured absorption rate using an appropriate theoretical expression. The jet device gives gas-liquid contact times in the range of 0.001 to 0.02 s and is appropriate for measuring the diffusivity of chlorine. The short contact time eliminates the effect of any liquid phase reaction on the absorption rate of Cl_2. Because of the significantly lower solubility of O_2 in peroxide solutions, a larger surface area is needed to obtain measurable absorption rates. The wetted-sphere absorber gives contact times in the range of 0.1 to 1.0 s.

2.0 SOLUBILITY

The solubility of a gas in a liquid cannot be measured directly when the gas reacts with the solution as in the case of Cl_2 in BHP. However, for the case of electrolytic solutions, Danckwerts (Ref. 1) gives a method of relating the gas solubility in the electrolyte solution to the solubility of the gas in the solvent at the same temperature. This solubility expression in terms of Henry's law constant is

$$\log_{10}(H/H^o) = h\,I \tag{2}$$

where H is Henry's law constant for the gas in the electrolyte solution, H^o is the value in the solvent and I is the ionic strength of the solution defined by

$$I = \frac{1}{2}\sum c_i\,z_i^2 \tag{3}$$

with c_i being the concentration of the ions of valency z_i. The quantity h is the sum of the contributions of the negative ions, the positive ions and the gas itself.

$$h = h_+ + h_- + h_G \tag{4}$$

In Equation 4, h_+ and h_- are constants and h_G is a function of temperature.

Since chlorine reacts in BHP its solubility cannot be measured directly. Also, BHP solutions are very unstable under normal conditions, with H_2O_2 decomposing to O_2 and H_2O. This makes it very difficult to measure the O_2 solubility volumetrically. For these reasons, it was attempted to

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...rry out measurements so that Equation 2 can be applied for the prediction of the physical solubility of chlorine and oxygen in BHP.

For most BHP solutions, in the concentration range of interest, the components are not completely in ionic form. According to the equilibrium constant for the dissociation reaction (Balej and Spalek, Ref. 2)

$$KOH + H_2O_2 \longrightarrow K^+ + OH^- + HOO^- + H^+ \tag{5}$$
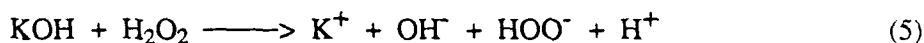
hydrogen peroxide is the main component in undissociated form, where the dissociated species are potassium ion (K^+), hydroxyl ion (OH^-), peroxyl ion (HOO^-), and hydrogen ion (H^+). Therefore, H^o may represent the solubility of the gas in hydrogen peroxide solution. The concentrations of the ions can be calculated from the equilibrium constant for the reaction in Equation 5 given by Balej and Spalek (Ref. 2). The h parameters for the ions in Equation 4 are reported by Danckwerts (Ref. 1). The parameters h_G for Cl_2 and O_2 can be calculated by measuring the solubility of each gas in a given solution and comparing this to the solubility of the same gas in water according to Equation 2.

The solubility experiments attempted in this work are: O_2 in H_2O, BHP and aqueous H_2O_2 solutions; Cl_2 in H_2O, aqueous KCl and H_2O_2 solutions. The objective of these experiments is to determine as many of the solubility parameters as possible for use in Equation 2.

2.1 EXPERIMENTAL APPARATUS AND PROCEDURE

The principal idea of the method used here is to bring a known volume of liquid into contact with a volume of gas in a closed system at constant temperature and pressure. Equilibrium is reached by agitating the liquid for some time until no change in the volume of the gas is observed. The amount of gas absorbed is measured volumetrically. The apparatus is shown in Figure 1. This apparatus was modified from our original solubility apparatus as described by Haimour and

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A From Gas Supply
B Constant Temperature Bath
C Absorption Flask
D Liquid Injection
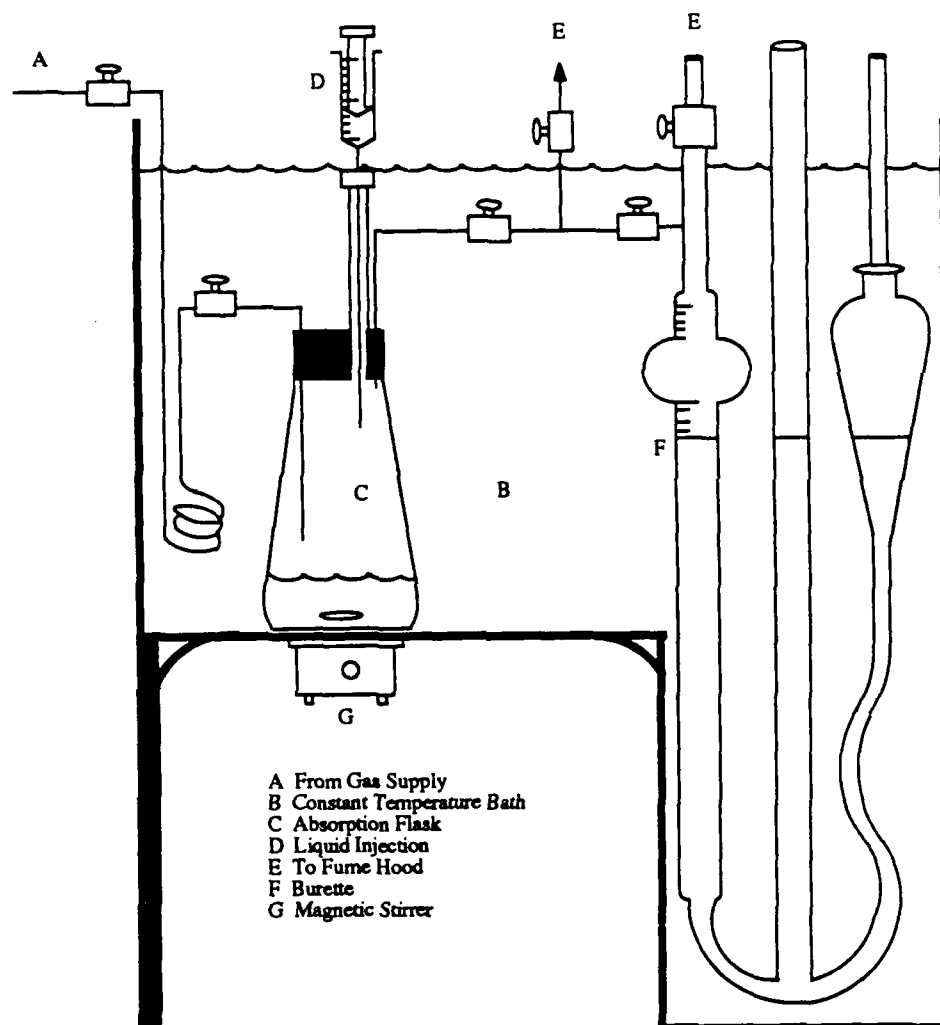E To Fume Hood
F Burette
G Magnetic Stirrer

Figure 1.   Solubility apparatus for oxygen.

Sandall (Ref. 3). The principle modification for this work was the addition of a spherical volume in the mercury burette. The sphere has a volume of 48.2 ml which allows a larger volume of liquid sample to be injected into the equilibrium cell and thereby increases the volume of gas absorbed at equilibrium. This modification was necessary for the experiments with O_2 because of its relatively low solubility.

Figure 2 shows a further modification to the solubility apparatus that was made for measurements using Cl_2. The Cl_2 reacted with mercury and several substitute manometer fluids, such as butyl phthalate, silicon oil, Meriam red and blue oil (brominated aromatics) and aqueous hydrochloric acid (HCl) solutions. The solution to this problem was to include two coils in the gas lines as shown in Figure 2. One coil, labeled (I) in Figure 2 (which initially contains air), delays the diffusion of chlorine to the mercury in the gas burette. The other coil, labeled (H) in Figure 2 (which initially contains Cl_2), is to insure that only Cl_2 is in contact with the liquid sample in the equilibrium cell.

The procedure for making a solubility measurement is as follows. A gas saturated with the vapors of the absorbing liquid is passed through the system at constant temperature long enough to completely purge the absorption flask. Then the inlet and outlet valves are closed. The heights of mercury in the three branches are leveled, ensuring that the pressure in the flask is atmospheric, and the position of the meniscus is recorded. An aliquot of degassed liquid which was kept at the same temperature as the experiment is weighed and then injected into the absorption flask. The liquid sample is continuously agitated via an external magnetic stirrer. The levels of mercury in the three branches are leveled every few minutes to make sure that the gas phase is at atmospheric pressure. Equilibrium is reached when the position of the meniscus in the burette (while the three branches are leveled) stops changing. The whole apparatus is kept at constant temperature inside a temperature controlled bath. The bath temperature variation is usually less than 0.05 °C during any given run.

A From Gas Supply
B Constant Temperature Bath
C Absorption Flask
D Liquid Injection
E To Fume Hood
F Burette
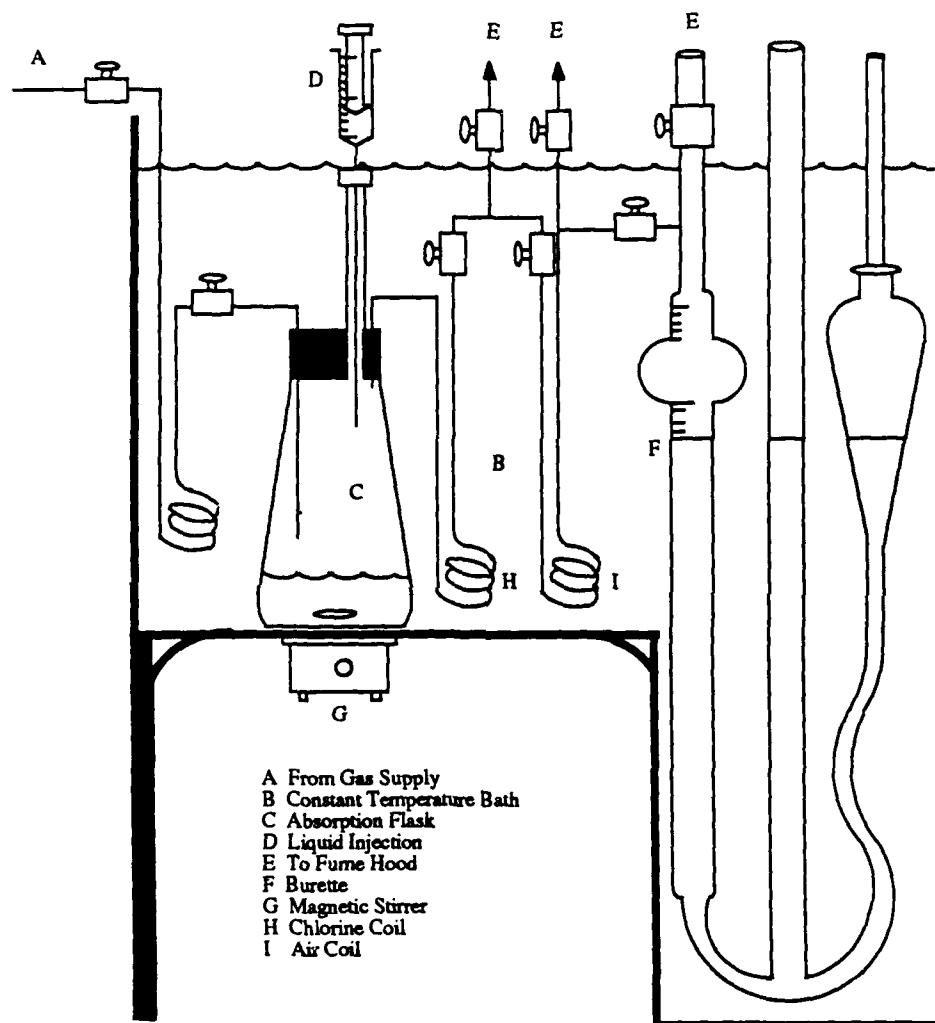G Magnetic Stirrer
H Chlorine Coil
I   Air Coil

Figure 2. Solubility apparatus for chlorine.

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The method of operation is as follows:

(a) The gas space in the absorption flask (C in Figure 2) is filled with gas that has been saturated with the liquid by flow through the saturation flask.

(b) After the gas in the absorption flask has been purged of all air. The gas valves are closed and a known volume of degassed liquid is injected into the absorption flask and the magnetic stirrer (G in Figure 2) is turned on.

(c) Equilibrium between the gas and the liquid is achieved in approximately 15 min. The pressure is maintained constant by adjustment of the manometer fluid reservoir.

(d) After equilibrium has been reached the difference in gas volume at constant pressure is measured on the gas burette (F in Figure 2) using a cathetometer.

(e) The volume of gas absorbed at equilibrium is equal to the volume of liquid sample added plus the volume change measured by the gas burette.

2.2 EXPERIMENTAL RESULTS

2.2.1 O_2 in H_2O

As a check on the experimental apparatus and procedure several measurements were carried out for O_2 solubility in water. Deionized distilled water was degassed under vacuum and the solubility of O_2 was measured in the apparatus. The volume of gas absorbed was converted to a molar concentration in the liquid according to

$$C_2 = (V_{ABS} P_T) / (V_l R T) \qquad (6)$$

where C_2 is the concentration of the gas absorbed in the liquid sample (gmol/l), V_{ABS} is the volume of gas absorbed (ml), P_T is the total pressure (atm), V_l is the volume of liquid sample (ml), R is the ideal gas constant (0.08205 atm l/gmol K), and T is the temperature (K). Then the solubility of the gas was calculated in terms of Henry's law constant as

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$$H = P_i / C_i \qquad (7)$$

where P_i is the partial pressure of the gas in the equilibrium cell (atm) and C_i is the concentration of the dissolved gas in equilibrium with the liquid at the given temperature (gmol/l). Although the degasification of the liquid sample was done under a pressure (vacuum) of 0.34 atm, the concentration of oxygen in equilibrium with the liquid at that pressure (C_1) cannot be neglected compared with C_2. Therefore, the solubility in Equation 7 is corrected as described in Appendix A, and is given by

$$H = (P_T - P_w^{yap} - 0.052) / C_2 \qquad (8)$$

where P_w^{yap} is the water vapor pressure at the temperature of the experiment (atm). The results are shown in Figure 3 from which an average mean deviation of 1.58 percent is calculated when compared with values found in the literature (International Critical Tables, Ref. 4). The values for the solubility of O_2 in H_2O can be correlated by

$$\ln H = 12.8067 - \frac{1821.75}{T} \qquad (9)$$

which predicts the solubility with an average mean deviation of 0.07 percent. This equation is valid in the temperature range of 0 to 20 °C.

2.2.2 O_2 in BHP Solutions

BHP solutions of several concentrations (1 to 3 M KOH) were prepared but no measurement of solubility could be achieved because of the high instability of these solutions. H_2O_2 decomposes to oxygen making the volumetric determination impossible. The addition of a stabilizer (oxine) was also attempted with unsuccessful results.
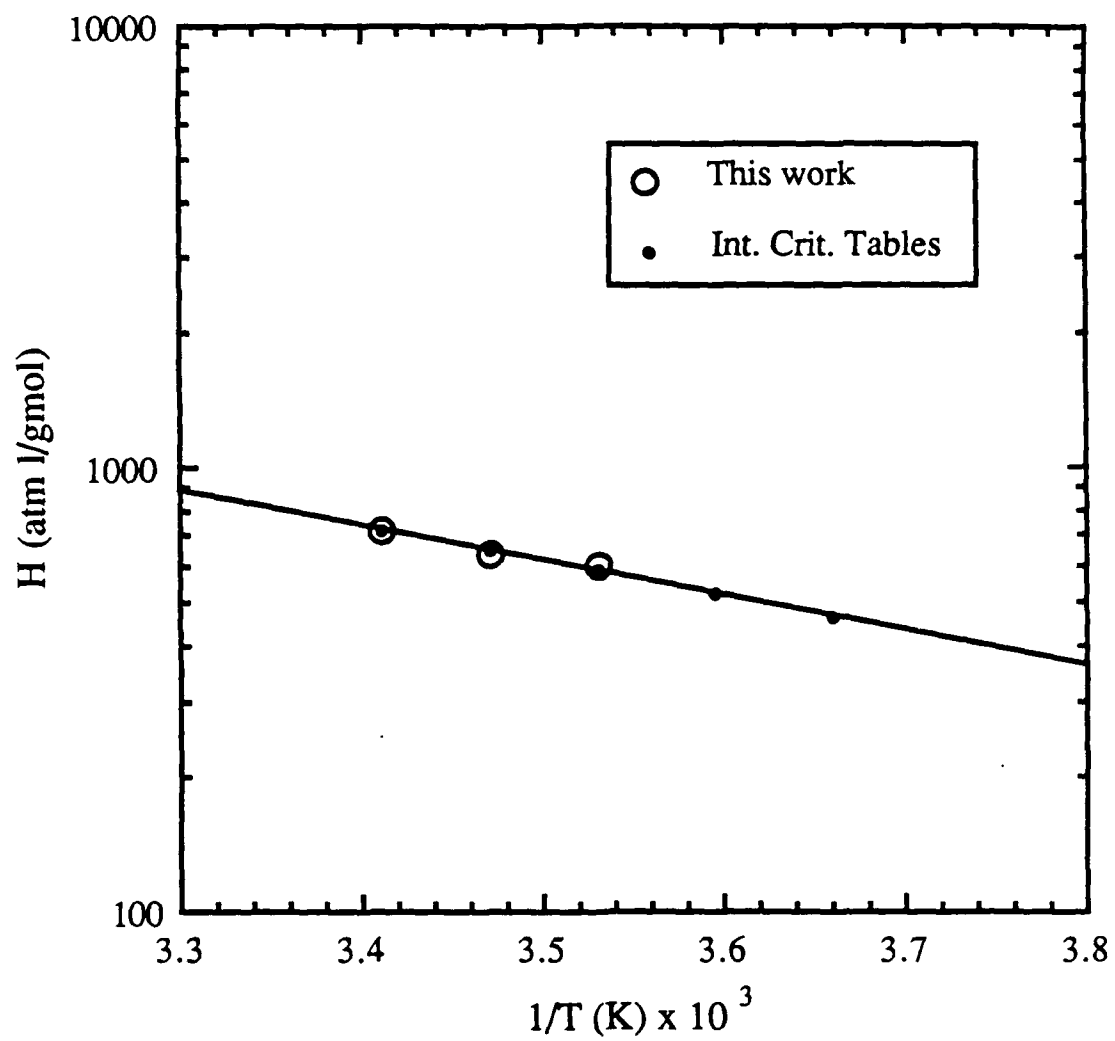
Figure 3. Solubility of oxygen in water.

2.2.3 O_2 in Aqueous H_2O_2 Solutions

A solution of 35 percent (wt) H_2O_2 was prepared from deionized distilled water and 90 percent (wt) H_2O_2. Oxine was added to the solution as a stabilizer in the concentration of 1 ml per liter of solution to avoid the decomposition reaction. It is believed that the small concentration of this chemical does not change the properties of the solution. The samples were kept under vacuum to degas them before injection into the equilibrium cell. A sample was weighed in an analytical balance and its volume (V_1) was determined from its density. The values of the density of H_2O_2 solutions were determined from Schumb, et al. (Ref 5). The volume of the gas absorbed (V_{ABS}) was measured with the apparatus and the concentration of O_2 absorbed by the liquid sample (C_2) was calculated according to Equation 6. The solubility was then calculated (see Appendix A) by

$$H = (P_T - 0.8\ P_w^{vap} - 0.322) / C_2 \tag{10}$$

The results are shown in Figure 4 and the average of the values at every temperature are shown in Table 1. The solubility of O_2 in 35 percent (wt) H_2O_2 can be correlated by

$$\ln H = 15.6255 - \frac{2586.66}{T} \tag{11}$$

TABLE 1. Solubility Of O_2 in 35 percent (wt) H_2O_2.

T (K)	H (atm l/gmol)
291.95	871.0
283.65	697.8
276.75	504.5
269.55	432.6
263.45	332.0

Figure 4. Solubility of oxygen in 35 percent (wt) hydrogen peroxide.
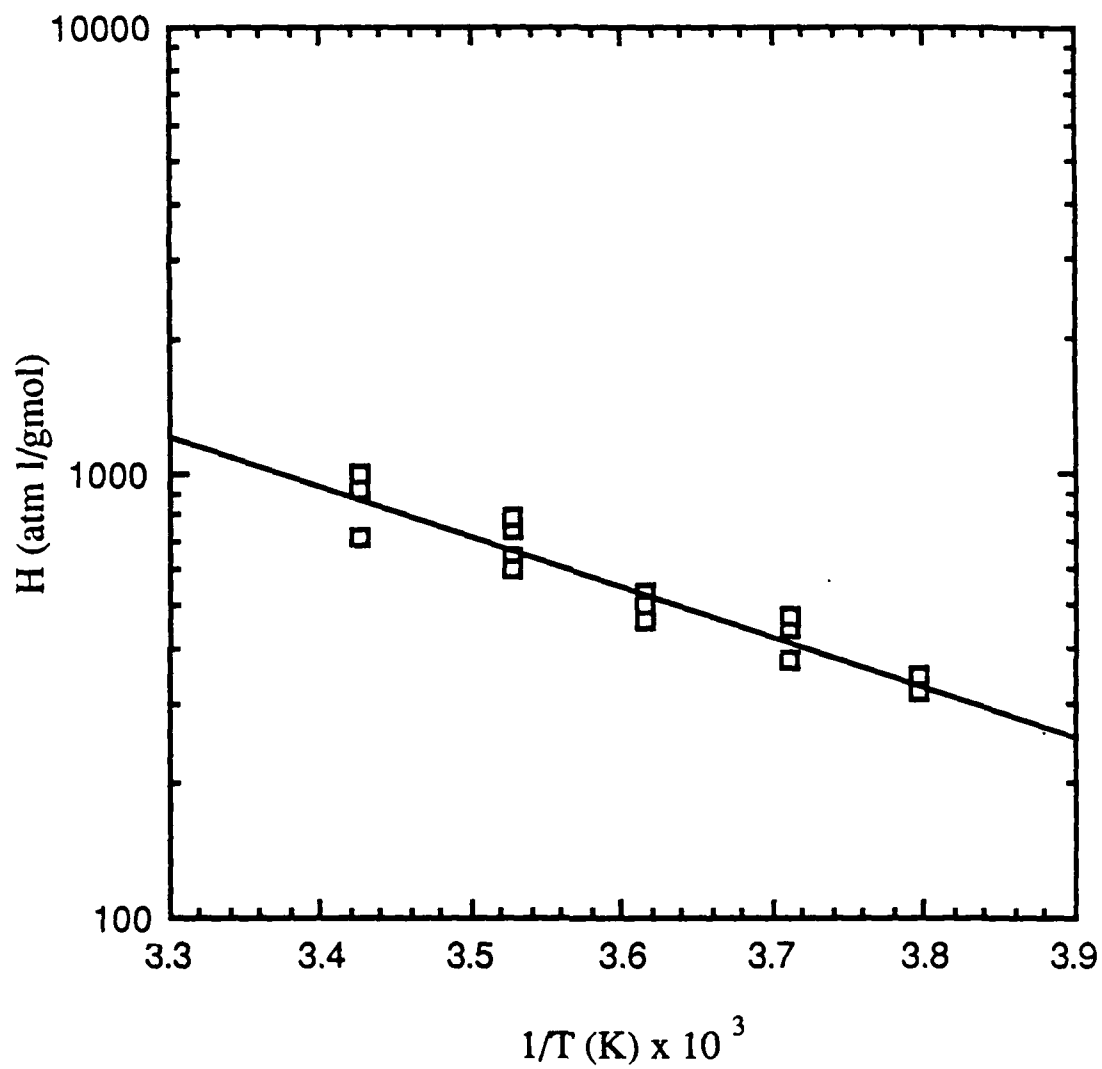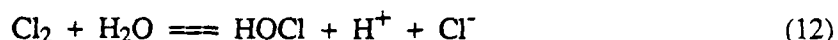
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which predicts the experimental values with an average mean deviation of 1.3 percent. This correlation is valid in the temperature range of -10 to 20 °C.

2.2.4 Cl_2 in H_2O

When Cl_2 is absorbed in water the following hydrolysis reaction occurs

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{12}$$

where the products are hypochlorous acid (HOCl), hydrogen ion (H^+) and chlorine ion (Cl^-). Whitney and Vivian (Ref. 6) measured the equilibrium constant for this reaction and the physical solubility of Cl_2 in water. From equilibrium calculations it may be shown (see Appendix B) that by adding HCl to water to give a concentration of 0.1 N HCl, the hydrolysis reaction will be suppressed and the physical solubility can then be measured in the solubility apparatus. Table 2 and Figure 5 give the experimental results of this work. Figure 5 also shows the data of Whitney and Vivian plotted as H versus 1/T. The data of this work show very good agreement with the Whitney and Vivian data, with an average mean deviation of 2.80 percent. The Whitney and Vivian data can be correlated by

$$\ln H = 14.124 - \frac{3384.1}{T} \tag{13}$$

2.2.5 Cl_2 in Aqueous KCl

Solubility measurements for Cl_2 in aqueous KCl were carried out to determine h_{Cl_2} as a function of temperature. 1 N KCl solutions were prepared with HCl added to give 0.1 N HCl. The HCl was added to limit the hydrolysis reaction. The solutions were degassed under vacuum and the solubility of Cl_2 was measured as a function of temperature. The data are given in Table 3 and are shown plotted in Figure 6. This figure also shows the correlation line given by the equation

$$\ln H = 12.336 - \frac{2832.87}{T} \tag{14}$$

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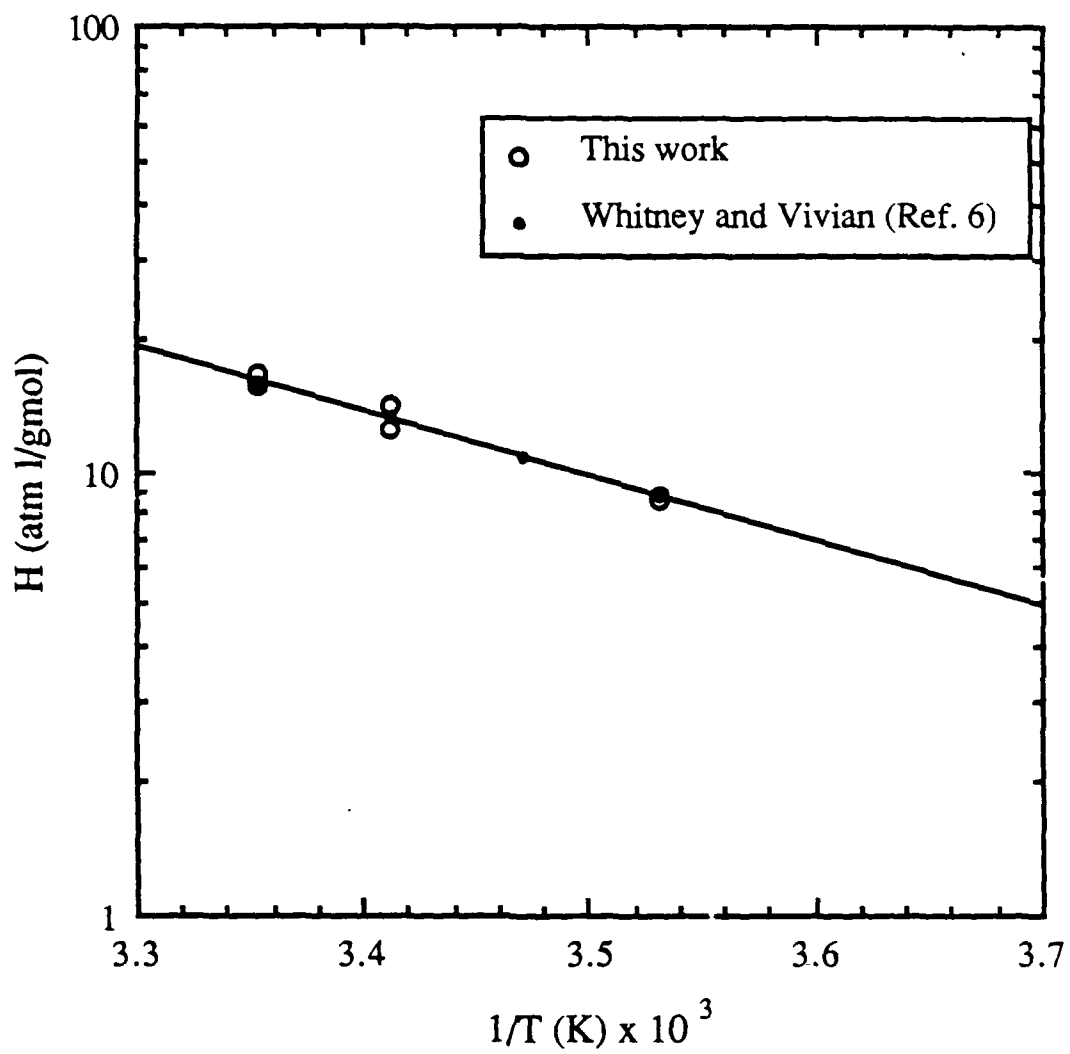
Figure 5. Solubility of chlorine in water.

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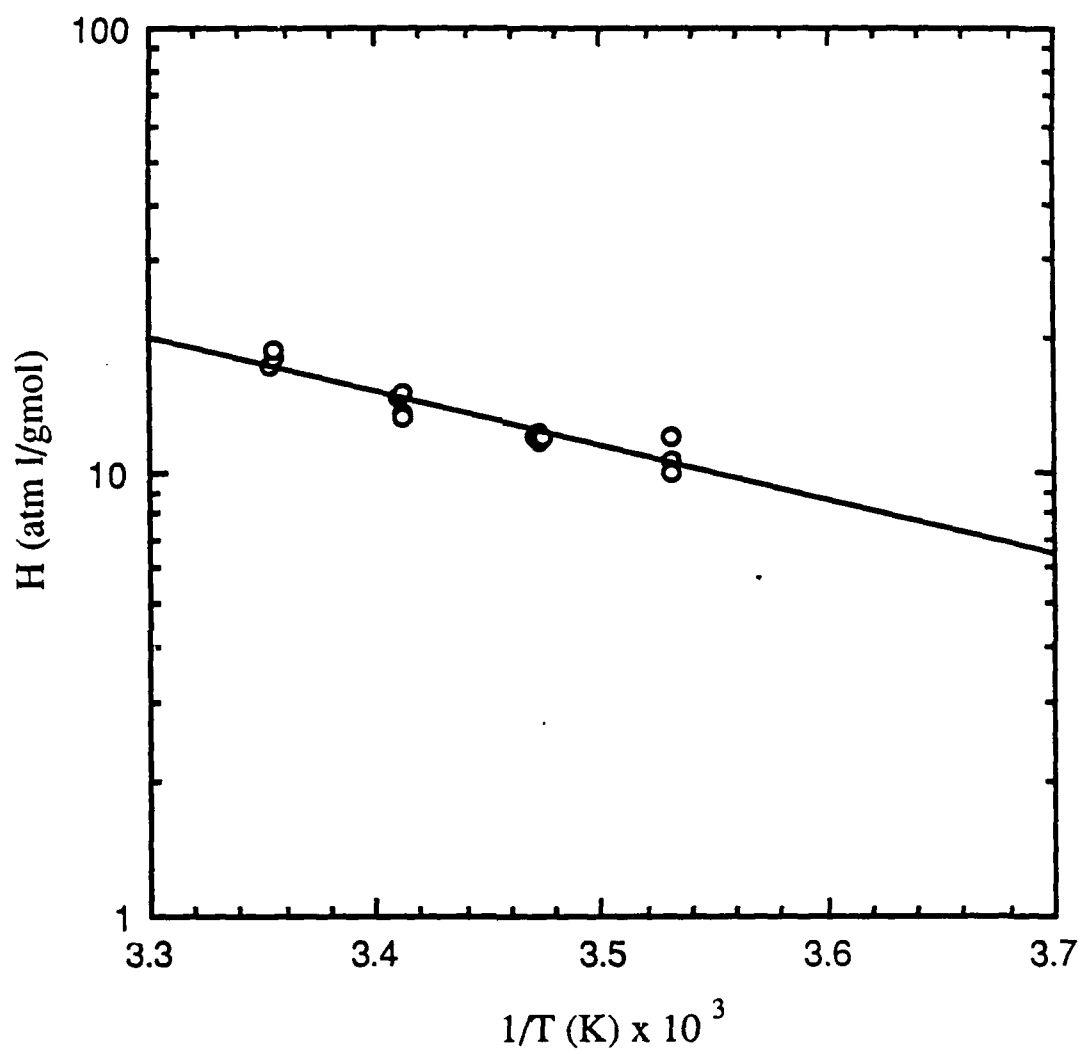
Figure 6. Solubility of chlorine in aqueous 1 N KCl.

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TABLE 2. Solubility of chlorine in water.

T (K)	H (atm l/gmol)	Reference
283.15	8.83	Whitney and Vivian[a]
283.15	8.80	This work
283.15	8.62	This work
288.15	10.69	Whitney and Vivian[a]
293.15	13.31	Whitney and Vivian[a]
293.15	14.10	This work
293.15	12.5	This work
298.15	16.01	Whitney and Vivian[a]
298.15	16.40	This work
298.15	15.76	This work
298.15	15.62	This work
298.15	15.82	This work

a Reference 6.

TABLE 3. Solubility of chlorine in aqueous KCl.

T (K)	H (atm l/gmol)
283.15	10.73
288.15	11.91
293.15	13.97
298.15	17.92

2.2.6 Cl_2 in Aqueous H_2O_2

Attempts were made to measure the solubility of Cl_2 in H_2O_2 solutions. These attempts were not successful because of the reaction which occurs between H_2O_2 and Cl_2 :

$$H_2O_2 + Cl_2 === O_2 + 2H^+ + 2Cl^- \qquad (15)$$
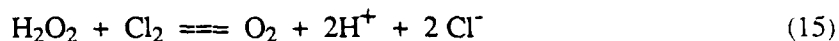
Thus, when Cl_2 is brought into contact with aqueous H_2O_2 the reaction of Equation 15 occurs in solution and O_2 gas is evolved. The equilibrium constant for this reaction (1.109×10^{24} at 25 ºC, Held, et al., Ref. 7) is sufficiently large that the reaction cannot be suppressed by the addition of HCl.

2.3 ESTIMATION OF SOLUBILITY PARAMETERS

In order to estimate the physical solubility of Cl_2 and O_2 in BHP, the solubility parameters for the following ions are needed: K^+, H^+, Cl^-, OH^-, and HOO^-. Also, h_{Cl_2}, and h_{O_2} are needed along with the H values for aqueous H_2O_2.

In this work, H_{O_2} was measured for 35 percent (wt) H_2O_2 as function of temperature (Eq. 11). As discussed in the previous section, attempts to measure H_{Cl_2} in H_2O_2 were not successful because of the reaction given by Equation 15. However, since it is found that, over the temperature range for this work, H_{O_2} for 35 percent (wt) H_2O_2 is only 1 to 19 percent higher than H_{O_2} for water by itself, a reasonable estimate for H_{Cl_2} in aqueous H_2O_2 would be

$$\frac{H_{Cl_2\text{-}H_2O_2}}{H_{Cl_2\text{-}H_2O}} = \frac{H_{O_2\text{-}H_2O_2}}{H_{O_2\text{-}H_2O}} \qquad (16)$$

From the solubility measurements of Cl_2 in aqueous KCl, h_{Cl_2} can be determined. For mixed electrolytes Danckwerts (Ref. 1) recommends that the gas solubility be estimated by

$$\log_{10}(H/H^0) = h_1 I_1 + h_2 I_2 + \cdots + h_i I_i \qquad (17)$$

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where I_i is the ionic strength of species i and h_i has the value characteristic of that electrolyte. Applying Equation 17 to the 1.0 M KCl / 0.1 M HCl solution used in this work, gives

$$\log_{10}(H/H^O) = (h_{K^+} + h_{Cl^-} + h_{Cl_2})(1) + (h_{H^+} + h_{Cl^-} + h_{Cl_2})(0.1) \tag{18}$$

Danckwerts gives the following values: $h_{K^+} = 0.074$, $h_{Cl^-} = 0.021$, $h_{H^+} = 0.000$. Using these values in Equation 18 together with the measured values of H and H^O at several temperatures, it is possible to calculate h_{Cl_2} as a function of temperature. These results are given in Figure 7 and Table 4. Hikita, et al. (Ref. 8) report values of h_{Cl_2} over the temperature range 20 to 50 °C. The Hikita, et al. values of h_{Cl_2} are also reported in Table 4. The value found in this work at the common temperature of 20 °C is -0.0520, compared to the value of -0.0145 reported by Hikita, et al. (Ref. 8). The values of h_{Cl_2} found in this work can be fitted to the following equation

$$h_{Cl_2} = (0.7449) - (2.72 \times 10^{-3})\, T \tag{19}$$

TABLE 4. Parameter h_{Cl_2} as a function of temperature.

T (K)	h_{Cl_2}	Reference
273.15	0.0024	This work
278.15	-0.0119	
283.15	-0.0258	
288.15	-0.0391	
293.15	-0.0520	
293.15	-0.0145	Hikita et al. (Ref. 8)
303.15	-0.0247	
315.15	-0.0296	
323.15	-0.0357	
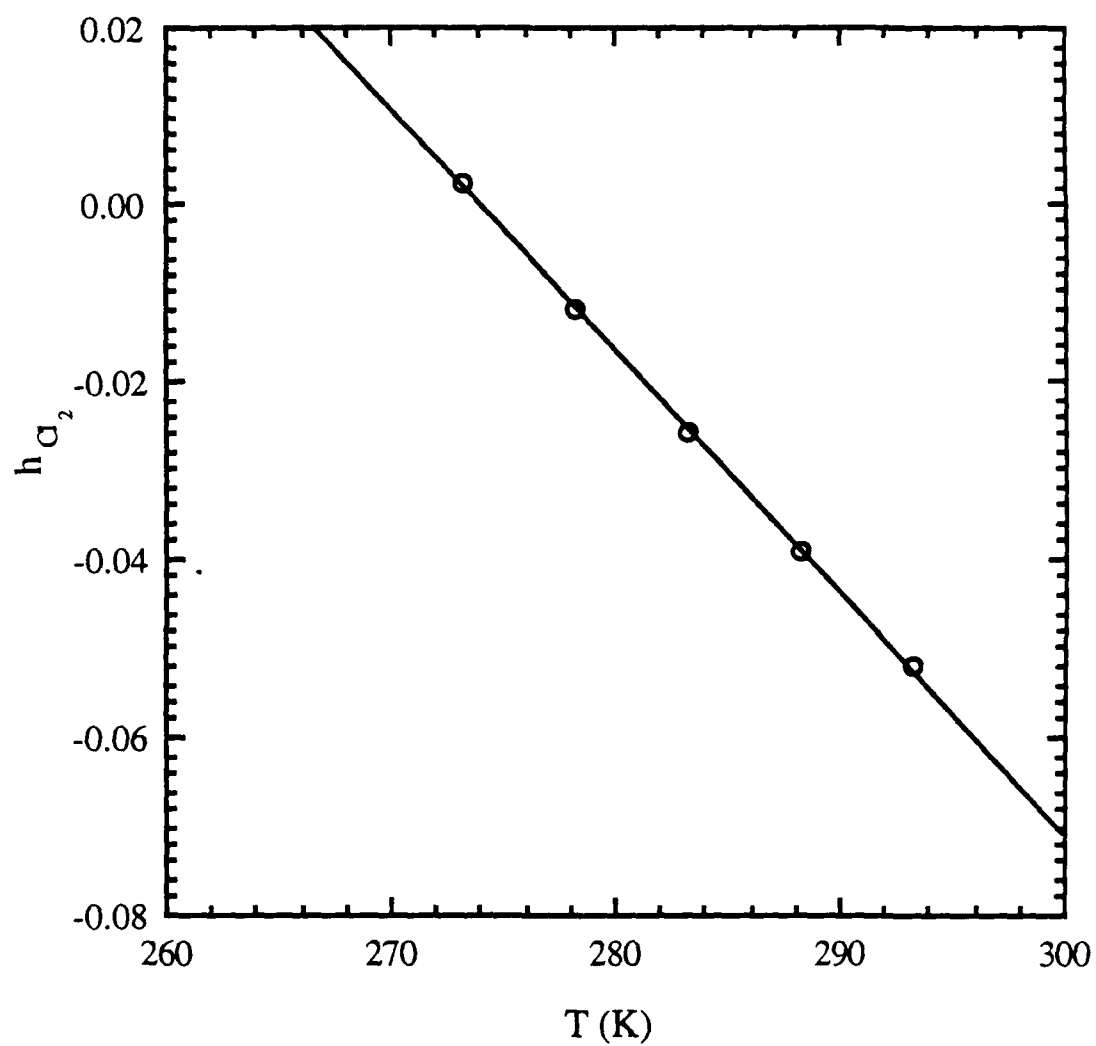
Figure 7. Parameter h for chlorine as a function of temperature.

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The parameter h_{O_2} is reported by Danckwerts (Ref. 1) at 15 and 25 °C. To extend the temperature range of h_{O_2}, data have been used from the International Critical Tables (Ref. 4) for the solubility of O_2 in 1 M NaCl. Application of Equation 2 to this system gives

$$\log_{10} (H/H^o) = (h_{Na^+} + h_{Cl^-} + h_{O_2})(1) \qquad (20)$$

Danckwerts gives $h_{Na^+} = 0.091$ and using the data for H from the International Critical Tables and calculating H^o from Equation 9, h_{O_2} was calculated for the temperature range 0 to 20 °C. These values are plotted in Figure 8 and tabulated in Table 5. The values calculated in this work for h_{O_2} are correlated by

$$h_{O_2} = (0.5426) - (1.6860 \times 10^{-3})\, T \qquad (21)$$

TABLE 5. Parameter h_{O_2} as a function of temperature

T (K)	h_{O_2}
273.15	0.0789
278.15	0.0754
283.15	0.0677
288.15	0.0587
293.15	0.0451

A value for h_{HOO^-} could not be determined in this work. However, Danckwerts (Ref. 1) suggests that when the value of the parameter h for an ion is not known, the value for a similar ion may be used. In this case it would be reasonable to assume that $h_{HOO^-} = h_{OH^-} = 0.066$.

Figure 8. Parameter h for oxygen as a function of temperature.

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3.0 DIFFUSIVITY

In this study, a laminar liquid jet absorber is used to measure the diffusion coefficient of chlorine gas in aqueous hydrogen peroxide s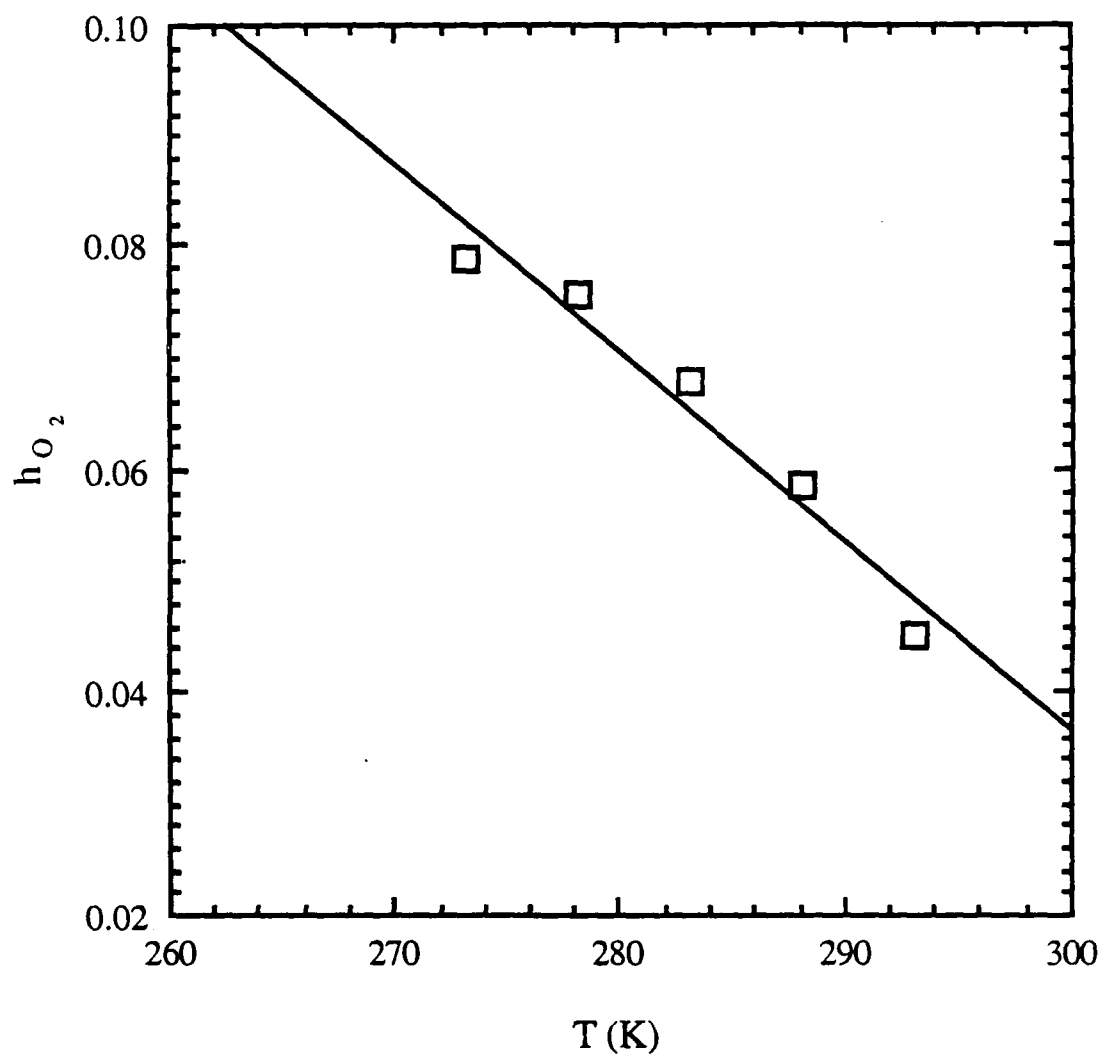olutions. These measurements can be used to estimate the diffusion coefficient of chlorine in alkaline hydrogen peroxide solutions. The technique involves the measurement of the gas absorption rate of Cl_2 gas into a flowing stream of liquid. The absorption data may be interpreted in terms of the Higbie Penetration Theory to give the liquid phase diffusion coefficient. The effect of chemical reaction on the rate of absorption is suppressed by operating at short gas-liquid contact times.

The laminar liquid jet apparatus provides a known surface area, well-defined hydrodynamics and a wide range of contact times. Absorption in laminar liquid jets has been shown to follow the penetration model very closely in previous gas absorption studies in this laboratory.

According to the penetration theory for a laminar jet (Haimour and Sandall, Ref. 3) the rate of gas absorption is given by

$$R_i = 4 \sqrt{D_i} \, C_i^* \sqrt{lq} \tag{22}$$

where R_i is the gas absorption rate (gmol/s), D_i is the diffusivity (cm^2/s), C_i^* is the saturation solubility of gas being absorbed (equal to P_i/H (gmol/ml)), l is the length of the jet (cm), and q is the volumetric flow rate (ml/s). Thus a plot of R_i against $\sqrt{lq}$ at constant temperature and pressure should give a straight line which passes through the origin and has a slope of $4 \, C_i^* \sqrt{D_i}$. Therefore,

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the product $C_i^* \sqrt{D_i}$ can be obtained from the slope. Knowledge of the solubility of the gas allows calculation of the diffusion coefficient.

It was found that the laminar liquid jet absorber is not suitable to measure the diffusivity of O_2 in aqueous H_2O_2. This is the case since the absorption rate for O_2 is not measurable in the jet apparatus because of the low solubility of O_2. The wetted-sphere absorber was used for these measurements since the sphere provides a much larger area for absorption and thus permits a measurable absorption rate.

Davidson and Cullen (Ref. 9) presented a solution for the problem of physical gas absorption by a laminar film flowing over a sphere. For a small depth of penetration, the rate of absorption (R_i) can be predicted by a series expansion of the form

$$R_i = L\,(C_i^* - C_i^0)\,[1.0 - \Sigma\,\beta_i\,\exp(-\gamma_i\,\alpha)] \tag{23}$$

where L is the liquid flow rate (ml/s), C_i^0 is the initial concentration of the gas in the liquid before the absorption (equal to zero for our case of degassed liquid), β_i and γ_i are constants given by Davidson and Cullen (Ref. 9), and α is defined as

$$\alpha = 3.36\,\pi\,\sqrt[3]{\frac{2\pi g}{3\nu}}\,r^{7/3}\,L^{-4/3}\,D_i \tag{24}$$

where $\pi=3.14159$, g is the acceleration due to gravity (9.8 m/s), ν is the kinematic viscosity of the liquid (cm^2/s), and r is the radius of the sphere (cm). Olbrich and Wild (Ref. 10) improved the general solution of Davidson and Cullen by adding more terms to the series. Note that the value of γ_7 is misprinted in the paper by Olbrich and Wild. The correct value as calculated from their Equation 19 is 461.8172.

The diffusivity can be calculated from the measured absorption rate, R_i, with Equation 23. An iterative calculation is required since D_i appears in the exponential.

3.1 DIFFUSIVITY OF Cl$_2$ IN AQUEOUS HYDROGEN PEROXIDE

A schematic drawing of the laminar liquid jet apparatus is shown in Figure 9. The absorption chamber is made of a 31 cm long, 7.6-cm inside diameter (i.d.) Pyrex glass cylinder and is enclosed by a constant-temperature jacket constructed from a 31 cm long, 16.5-cm i.d. Pyrex glass cylinder. Both cylinders are held between two stainless steel flanges and the ends are sealed with Teflon gaskets. Water to the jacket is supplied from and recycled to a constant-temperature circulating bath.

The liquid feed is pumped to a surge tank, then through a rotameter and through a coil in the constant-temperature jacket. It is then fed to a 1-cm i.d. delivery glass tube. The surge tank which is topped by a ·losed space of nitrogen gas helps in eliminating pump pulses. The delivery glass tube can slide in the vertical direction and can be locked in position by a swage-lock nut with teflon ferrules. The gas supply is fed through a coil in the constant-temperature jacket and is then introduced into the absorption chamber at the base and is exhausted at the top of the chamber.

The jet nozzle assembly is fitted onto the end of the glass delivery tube by two O-rings. The jet nozzle is a square-edged orifice, 0.051 cm in diameter, drilled in a thin sheet of polyvinyl chloride. This nozzle design was recommended by Raimondi and Toor (Ref. 11) for absorption rate results closest to the theoretical values for rodlike flow and no interfacial resistance. The receiver is a 1-cm i.d. glass tube fitted into a funnel-shaped base and capped by a Teflon plug in which a 0.1-cm hole is drilled. A hole in the base allows draining of any liquid overflow. The jet is centered by manipulating the mount of the delivery tube relative to the top flange. The jet is considered centered when all of its contents empty into the receiver with no overflow.

A leveling device consisting of a cup with an overflow drain is used to precisely adjust the liquid level in the receiver tube. If the level is low, gas entrainment occurs; if high, then the liquid overflows. The liquid level has to be readjusted after any changes in the liquid flow rate. The length of the jet is measured by a cathetometer with an error less than 5×10^{-3} cm.

A From Gas Supply
B From He Supply
C To Fume Hood
D Solution Supply
E Manometer
F Delivery Tube
G Jet Nozzle
H Absorption Chamber
I Water Jacket
J Receiver Tube
K Overflow
L To Drainage
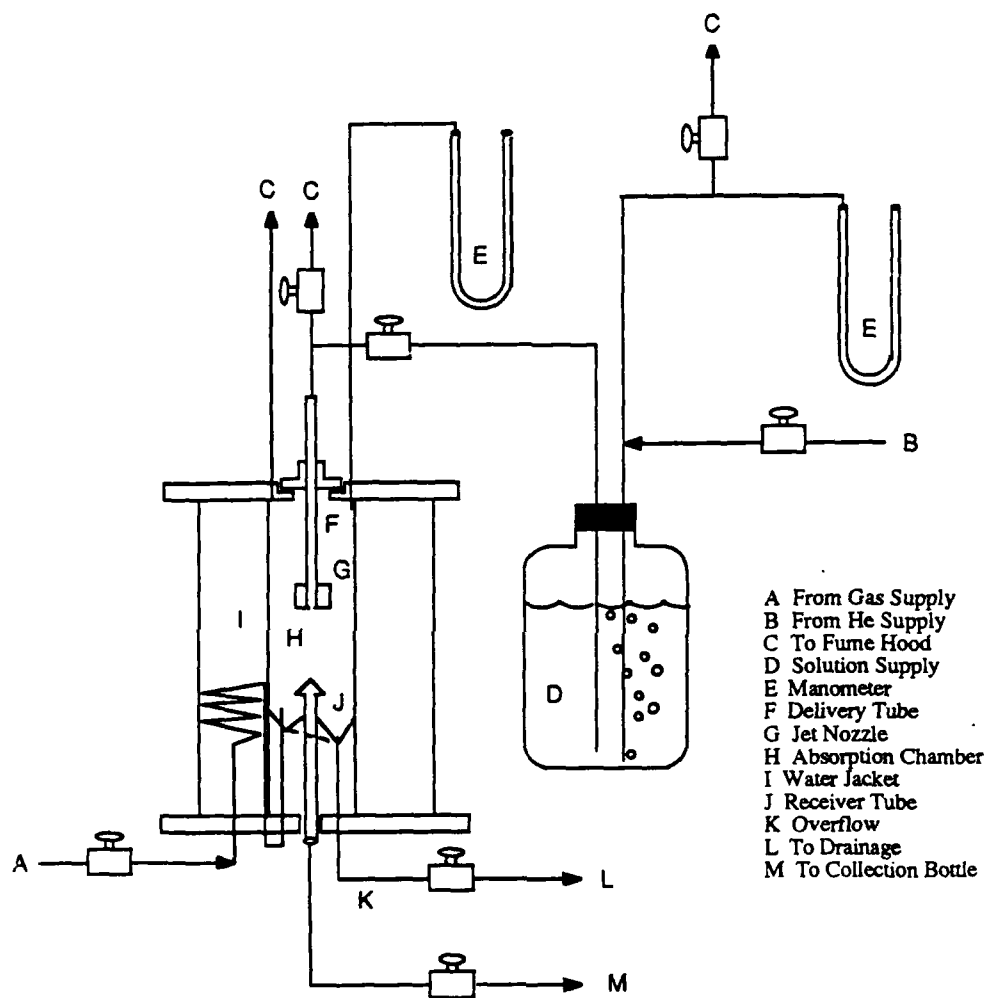M To Collection Bottle

Figure 9. Laminar liquid jet absorber.

The temperature of the system is monitored by thermometers in the constant-temperature jacket, in the jet chamber, and in the liquid delivery tube. The temperatures are controlled to within ± 0.30 °C.

The chlorine gas supply is turned on for enough time to displace all the air in the gas coil and the chamber. Measurements were taken after a stable jet flow was established. All of the experiments were done under atmospheric pressure.

In this study, the absorption rate of chlorine in 35 percent (wt) aqueous hydrogen peroxide was measured over a temperature range of -10 to 20 °C. The contact time in the jet apparatus was varied between 2.5×10^{-3} and 6.9×10^{-3} s. The absorption rates were measured by analysis of the outlet liquid stream for chloride ion concentration using a Fisher model 825 MP pH/mV/ion meter equipped with an Orion model 96-17B combination chloride ion electrode. The Fisher ion analyzer was calibrated with standard chloride solutions. The experimental data are presented in Table 6. The contact time was varied by changing the jet length and the liquid flow rate. The data are plotted in accordance with the penetration model in Figure 10. As expected, a straight line passing through the origin is obtained for each temperature. The product $C_i^* \sqrt{D_i}$ is obtained for each temperature from the slope of the straight lines. These values are reported in Table 7 along with the values of the diffusivity.

Calculation of the diffusion coefficients requires a knowledge of the solubility of chlorine in the liquid phase. C_i^* is calculated by the method recommended in the previous section.

$$H_{Cl_2-H_2O_2} = H_{Cl_2-H_2O} \frac{H_{O_2-H_2O_2}}{H_{O_2-H_2O}} \tag{25}$$

$$C_{Cl_2}^* = \frac{P_{Cl_2}}{H_{Cl_2-H_2O_2}} \tag{26}$$

Figure 11 shows a plot of the diffusivity values for chlorine in aqueous hydrogen peroxide.

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TABLE 6. Experimental data for Cl_2 - H_2O_2 absorption in the laminar liquid jet.

T (K)	l (cm)	q (cm³/min)	$\sqrt{lq}$ (cm²/min^{1/2})	$\sqrt{lq}$ (cm²/s^{1/2})	$R_i \times 10^7$ (gmol/s)
293.15	1.353	50.1	8.233	1.063	5.62
293.15	1.353	61.6	9.129	1.179	6.39
293.15	1.353	74.5	10.040	1.296	7.12
293.15	2.384	53.4	11.283	1.457	8.09
293.15	2.384	68.3	12.760	1.647	9.04
293.15	2.384	79.5	13.767	1.777	9.83
283.15	1.476	51.4	8.710	1.1245	8.92
283.15	1.476	58.6	9.300	1.2006	9.87
283.15	1.476	68.3	10.040	1.296	10.46
283.15	1.476	81.8	10.988	1.419	11.51
283.15	2.489	50.6	11.223	1.449	11.74
283.15	2.489	63.3	12.552	1.6205	12.93
283.15	2.489	76.9	13.835	1.7861	14.67
273.15	1.418	52.3	8.612	1.112	14.51
273.15	1.418	65.5	9.637	1.244	16.82
273.15	1.418	78.7	10.564	1.364	18.48
273.15	2.344	51.4	10.976	1.417	18.83
273.15	2.344	68.1	12.634	1.631	21.51
273.15	2.344	81.2	13.796	1.7811	23.95
263.15	1.502	54.5	9.048	1.168	2.19
263.15	1.502	66.3	9.979	1.288	2.55
263.15	1.502	79.5	10.927	1.411	2.63
263.15	2.445	50.2	11.079	1.430	2.84
263.15	2.445	70.3	13.110	1.6925	3.22
263.15	2.445	82.1	14.168	1.829	3.56

TABLE 7. Diffusivity of Cl_2 in 35 percent (wt) H_2O_2.

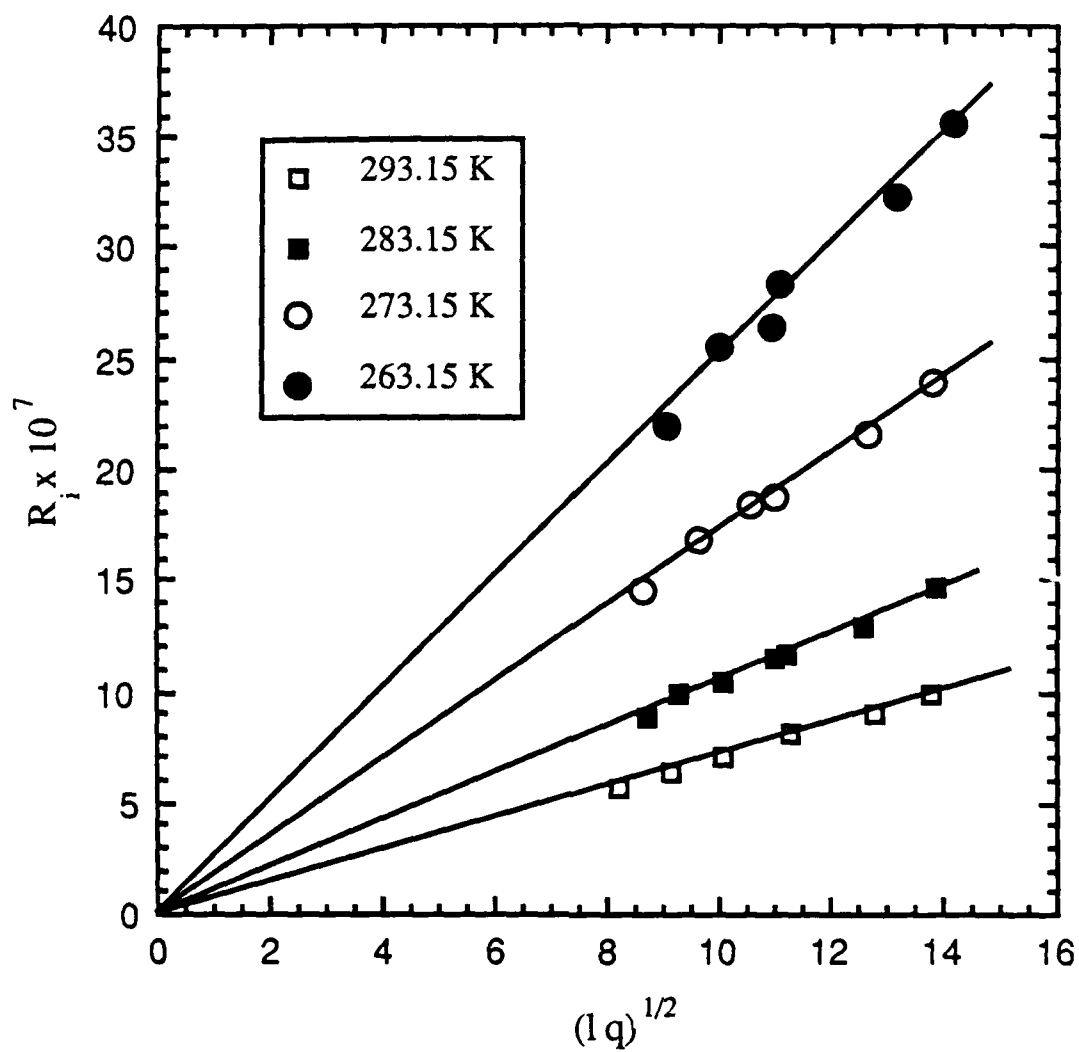| T (K)	Slope $\times 10^7$	$C_i^* \sqrt{D_i} \times 10^7$	$D_i \times 10^6$ (cm²/s)
293.15	5.47	1.37	4.99
283.15	8.05	2.01	3.94
273.15	13.00	3.25	3.53
263.15	19.08	4.77	2.40

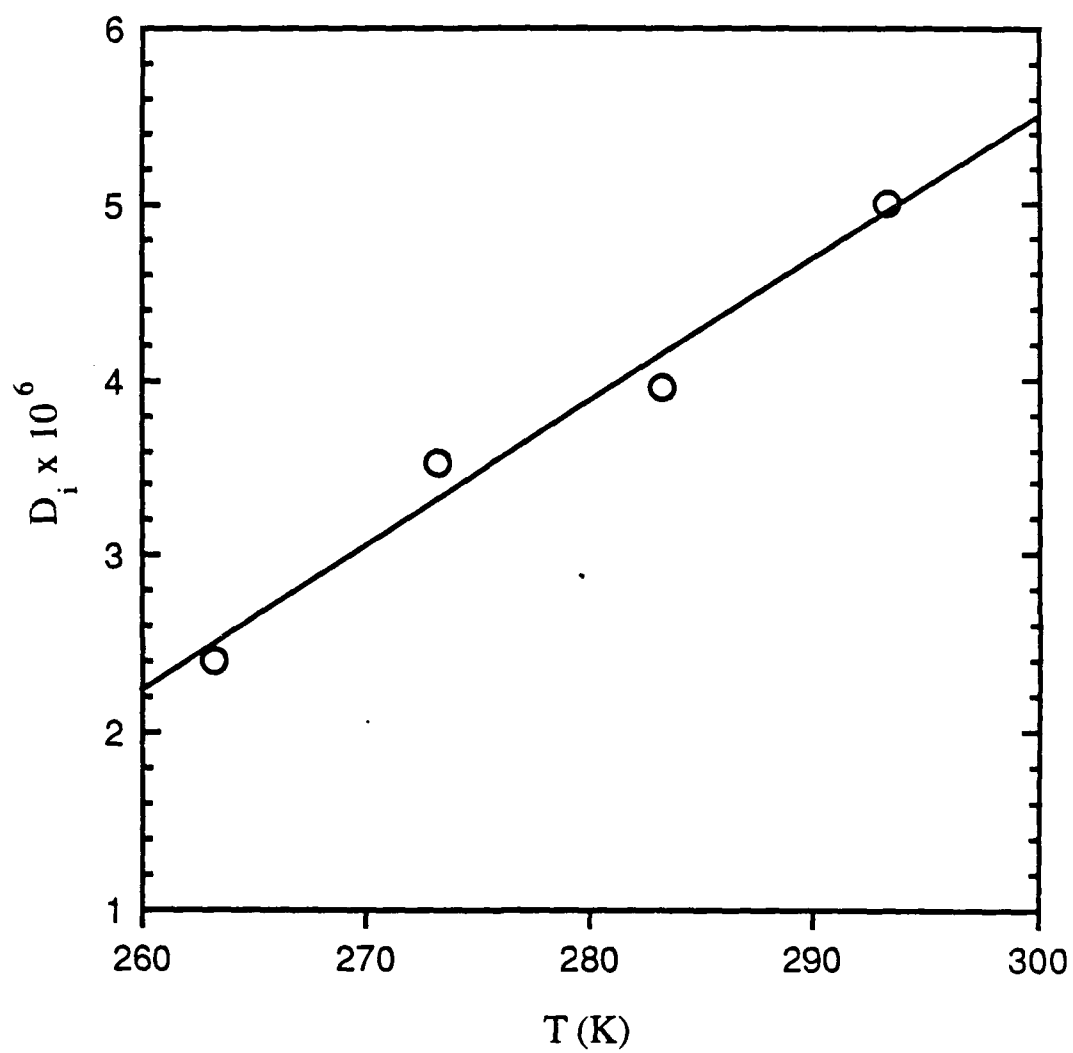Figure 10. Absorption of chlorine in the laminar liquid jet.

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Figure 11. Diffusion coefficient of chlorine as a function of temperature.

3.2 DIFFUSIVITY OF O_2 IN AQUEOUS H_2O_2

Several attempts were made to measure the diffusivity of O_2 in aqueous H_2O_2 using the laminar liquid jet apparatus. The absorption rates could not be measured in this apparatus because of the low solubility of oxygen. A wetted-sphere device as shown schematically in Figure 12 was used for these measurements. The wetted-sphere apparatus was modified from previous research (Al-Ghawas, et al. Ref. 12) in that a pressure feed was used for the liquid rather than a pump. This modification was made to minimize any decomposition of the hydrogen peroxide.

The dimensions and construction materials of the apparatus are the same as those of the laminar liquid jet apparatus, which is described earlier. The difference is the sphere assembly. The sphere, a Hastelloy ball of 3.76 cm diameter, was mounted on a 0.4-cm-diameter Hastelloy rod. The part of the rod above the sphere was accurately centered in the orifice of the liquid feed distributor. The liquid feed enters at the top and passes through the alignment block via eight holes which ensure even flow out of the orifice. After passing over the sphere the liquid runs down a short length of rod into a 0.9-cm i.d. receiving tube. The liquid is maintained at the top of this tube by a constant level device.

The sphere is fixed at 0.3 cm from the liquid feed orifice. This distance was chosen because at longer distances the liquid tended to break away from the rod and produced uneven distribution over the sphere. This condition is undesirable since it would alter the contact time and surface area by unpredictable amounts. At shorter distances, the liquid tended to spray out over the ball even at moderate flow rate. The length of the rod between the sphere and the receiving tube was fixed at 2.0 cm, since it was found experimentally by Davidson and Cullen (Ref. 9), Goettler (Ref. 13), Wild and Potter (Ref. 14), and Tomcej et al. (Ref. 15) that for distances less than 2.0 cm the rate of absorption drops appreciably because of a stagnant layer end effect. When the distance was greater than 2.0 cm, rippling effects became significant.

A   From Gas Supply
B   From He Supply
C   To Fume Hood
D   Solution Supply
E   Manometer
F   Liquid Distributor
G   Wetted Sphere
H   Absorption Chamber
I   Water Jacket
J   Receiver Tube
K   Overflow
L   To Drainage
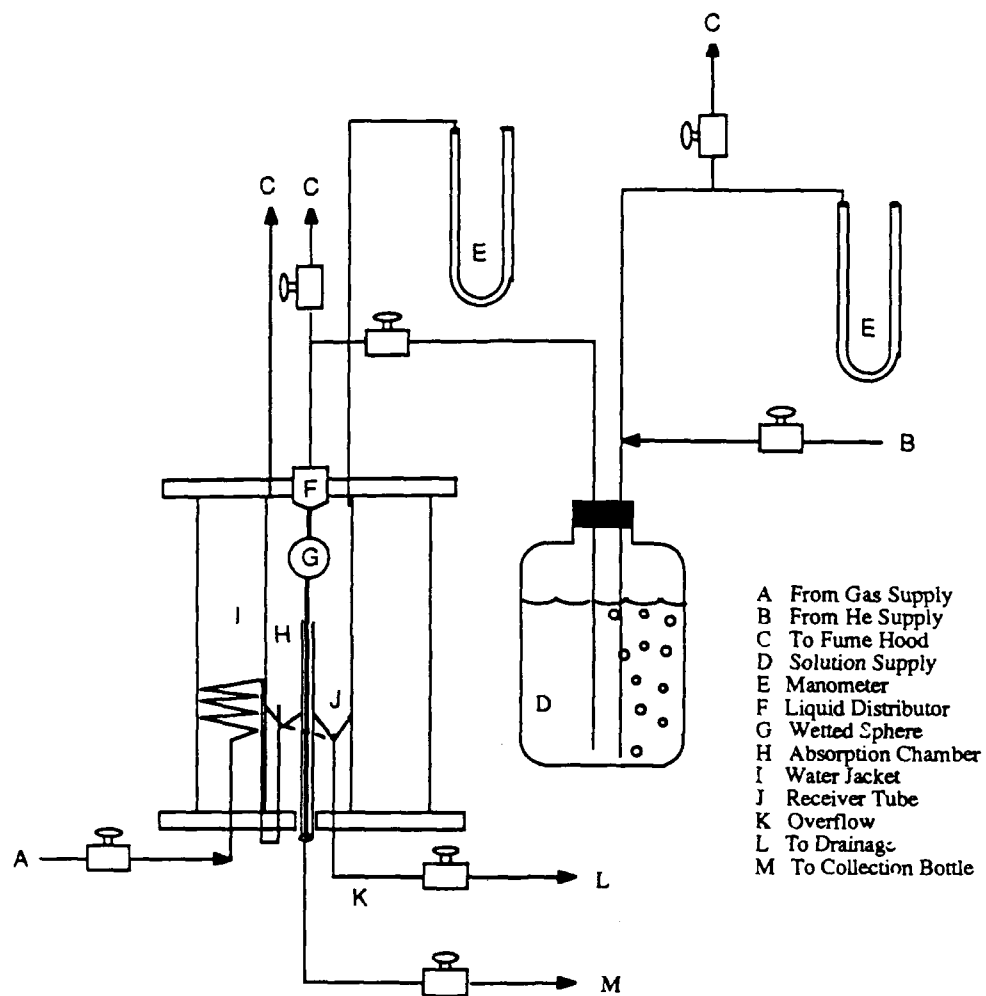M   To Collection Bottle

Figure 12. Wetted-sphere absorber.

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Freshly degassed liquid is initially fed to the distributor at high flow rates to ensure complete wetting of the sphere. When the liquid film has stabilized the flow rate is reduced to the desire rate. After the liquid film is flowing satisfactorily, the gas is turned on for enough time to purge the absorption chamber and for all the tubing to fill with the gas. The gas is then turned off and the rate of gas absorption is found by measuring the amount of time needed for a soap film to travel through a fixed volume.

All of the experiments were done under atmospheric pressure. The temperature of the system was monitored by thermometers in the constant-temperature jacket, in the absorption chamber, and in the liquid feed distributor. The temperature was controlled to within ± 0.3 °C.

As a check on the operation of the apparatus, the diffusivity of oxygen in water at 12 °C was measured. A value of 1.41×10^{-5} cm^2/s was found. This may be compared to 1.45×10^{-5} cm^2/s determined by Baird and Davidson (Ref. 16) using a sphere absorber and 1.40×10^{-5} cm^2/s determined by Baird and Davidson using a jet absorber.

Table 8 gives the data obtained over the temperature range -8 to 12 °C for the diffusivity of oxygen in 35 percent (wt) H_2O_2. The data are shown plotted in Figure 13. The experimental data are correlated by

$$D = -1.6552 \times 10^{-4} + 6.3259 \times 10^{-7} T \tag{27}$$

3.3 ESTIMATION OF DIFFUSIVITY FOR OTHER SOLUTION CONCENTRATIONS AND TEMPERATURES

Most predictive equations for the diffusion coefficient of gases in liquids, such as the Akgerman and Gainer Equation (Ref. 17), are based on the Stokes-Einstein theory.

$$\frac{D\,\mu}{T} = \text{a constant} \tag{28}$$

Thus, a method of estimating the diffusivity at another temperature or concentration would be

$$D_2 = \frac{T_2}{T_1} \frac{\mu_1}{\mu_2} D_1 \qquad (29)$$

In Equation 29, D_1 is the known value of the diffusivity at temperature T_1 and viscosity μ_1, and D_2 is the desired value of the diffusivity at T_2 and μ_2. The effect of any concentration change on the predicted diffusivity is taken into account through the viscosity μ_2.

TABLE 8. Diffusivity of O_2 in 35 percent (wt) H_2O_2.

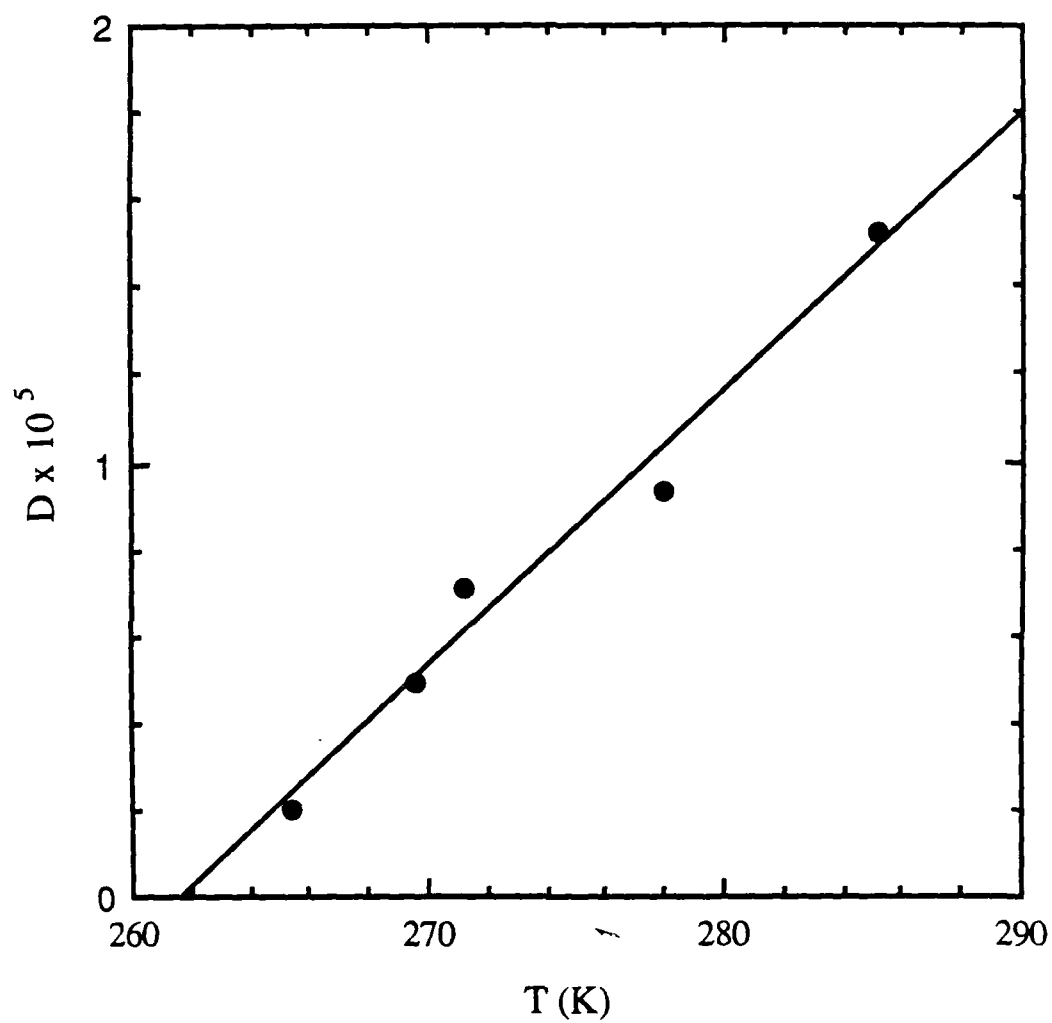| T (K)	D x 10^5 (cm^2/s)
285.15	1.52
277.95	0.93
271.15	0.71
269.55	0.49
265.35	0.20

Figure 13. Diffusion coefficient of oxygen as a function of temperature.

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ACRONYMS

BHP   Basic Hydrogen Peroxide

NOMENCLATURE

c_i Concentration of the ions in the solution (gmol/l)

C_1 Concentration of gas in equilibrium with liquid at degasification (gmol/l)

C_2 Concentration of the gas absorbed by liquid sample (gmol/l)

C_i Concentration of dissolved gas in liquid (gmol/l)

C_i^* Saturation solubility of gas being absorbed (gmol/l)

C_i^0 Initial concentration of gas in liquid (gmol/l)

Cl_2 Chlorine

Cl^- Chloride ion

D_i Diffusivity of gas i (cm^2/s)

g   Acceleration of gravity (9.8 m/s)

h   Solubility parameter defined in Equation 4

h_+ Solubility parameter for the positive ions in solution

h_- Solubility parameter for the negative ions in solution

h_G Solubility parameter for gas G defined in Equation 4

H   Henry's law constant the gas in the liquid solution (atm l/gmol)

H^o Henry's law constant for the gas in the solvent (atm l/gmol)

H^+ Hydrogen ion

H_2O Water

H_2O_2 Hydrogen Peroxide

HOCl   Hypochlorous acid

HOO^-	Peroxyl ion
HCl	Hydrochloric acid
I	Ionic strength of the solution defined by Equation 3
K^+	Potassium ion
KCl	Potassium chloride
KOH	Potassium hydroxide
L	Liquid flow rate in the sphere absorber (ml/s)
l	Length of the liquid Jet (cm)
M	Molar concentration (gmol/l)
Na^+	Sodium ion
$NaCl$	Sodium chloride
$O_2(^1\Delta_g)$	Singlet Delta Oxygen
OH^-	Hydroxyl ion
P_i	Partial pressure of the gas in equilibrium with liquid (atm)
P_T	Total pressure (atm)
P_w^{vap}	Water vapor pressure (atm)
P_{vac}	Vacuum pressure used to degas liquid samples (0.342 atm)
q	Volumetric flow rate (ml/s)
r	Radius of the sphere (1.897 cm)
R	Ideal gas law constant (0.08205 atm l/gmol K)
R_i	Gas absorption rate (gmol/s)
T	Temperature (K)
V_{ABS}	Volume of gas absorbed (ml)
V_l	Volume of liquid sample (ml)
x_{O_2}	Mol fraction of oxygen in air
z_i	Valency of the ions in solution

Greek Symbols

α	Variable defined in Equation 24
β	Constant given in Olbrich and Wild (Ref. 10)
γ	Constant given in Olbrich and Wild (Ref. 10)
μ	Dynamic viscosity (Poise)
π	Constant = 3.14159
ν	Kinematic viscosity (cm^2/s).

APPENDIX A
SOLUBILITY CALCULATIONS

The solubility of a gas in a liquid is defined in terms of Henry's law constant, H (atm l/gmol), as

$$H = P_i / C_i \qquad \text{(A-1)}$$

where P_i is the partial pressure of the gas (atm) in the equilibrium cell and C_i is the total

concentration (gmol/l) of dissolved gas in equilibrium with the liquid at a given temperature. When

the liquid sample is degassed under vacuum there may be a significant concentration of the gas in

equilibrium with the liquid, C_1 (gmol/l), depending on the vacuum pressure. Under these

conditions the solubility of the gas may be expressed as

$$H = x_{O2} P_{vac} / C_1 \qquad \text{(A-2)}$$

where P_{vac} is the vacuum pressure, equal to 0.342 atm in our case, and $x_{O2} = 0.21$ is the mol

fraction of oxygen in air. C_i in Equation A-1 is the sum of C_1 and the experimentally measured C_2,

or in terms of Henry's law constant

$$H = P_i / (C_1 + C_2) \qquad \text{(A-3)}$$

P_i is equal to the total pressure minus the vapor pressure of the liquid at the temperature of the

experiment. Similarly the partial pressure in Equation A-2 has to be corrected for the vapor

pressure of the liquid at the temperature at which the liquid sample was degassed. For the case of water the vapor pressure at 20 °C is 0.02 atm. Therefore, Equations A-2 and A-3 can be written as

$$H = (0.21\ P_{vac} - 0.02)\ /\ C_1 \qquad\qquad (A-4)$$

and

$$H = (P_T - P_w^{vap})\ /\ (C_1 + C_2) \qquad\qquad (A-5)$$

From these two equations we can solve for C_1 and H to finally express Henry's law constant for the solubility of oxygen in water as

$$H = (P_T - P_w^{vap} - 0.052)\ /\ C_2 \qquad\qquad (A-6)$$

Similarly, for 35 percent (wt) hydrogen peroxide aqueous solutions the solubility can be calculated from

$$H = (P_T - 0.8\ P_w^{vap} - 0.322)\ /\ C_2 \qquad\qquad (A-7)$$

where it is assumed that Raoult's law holds and the water vapor pressure has been multiplied by the mol fraction of water in the solution. Also, the mol fraction of oxygen above the liquid sample during degasification has been taken as unity. It may be shown that the vapor pressure of H_2O_2 above the solution is negligible and is therefore neglected in Equation A-7.

APPENDIX B
SUPPRESSION OF CHLORINE HYDROLYSIS REACTION

Chlorine hydrolyzes in water according to

$$Cl_2 + H_2O === HOCl + H^+ + Cl^-$$ (B-1)
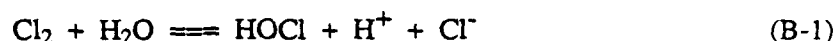
To calculate the extent of hydrolysis in 0.1 N HCl solution, the equilibrium constants found by Connick and Chia (Ref. B-1) are used. The activity coefficients used are those calculated by Kielland (Ref. B-2). At 0.1 N HCl these coefficients are: for H^+, 0.83, and for Cl^-, 0.755. The ratio of the activity coefficients for HOCl to that of H_2O is taken as unity by Connick and Chia (Ref. B-1) and this assumption is made here also.

Therefore, at 25 °C and one atmosphere total pressure

$$\frac{(0.83) [H^+] (0.755) [Cl^-] [HOCl]}{[Cl_2]} = 3.944 \times 10^{-4}$$ (B-2)

Under these conditions 0.0585 moles of chlorine dissolves in one liter of 0.1 N HCl (Spalding, Ref. B-3).

Making a material balance

$$[H^+] = 0.1 + [HOCl]$$ (B-3)

$$[Cl^-] = 0.1 + [HOCl]$$ (B-4)

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$$[Cl^-] + [HOCl] + 2[Cl_2] = 0.217 \qquad\qquad (B\text{-}5)$$

Solving for [HOCl] gives 0.0034 M which means 5.8 percent of the chlorine hydrolyzed. At lower temperatures even less chlorine will be hydrolyzed because of the decreasing equilibrium constant with decreasing temperature.